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ENVIRONMENT

OCCURRENCE OF ARSENIC IN GROUNDWATER NEAR COLD LAKE, ALBERTA

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EXECUTIVE SUMMARY

There are several areas in Alberta where well water samples contain elevated and undesirable levels of dissolved arsenic. One such area is the Cold Lake region. A well water testing program conducted by Alberta Health and Wellness in 1999 showed several samples from shallow domestic wells on properties located near Crane Lake and Hilda Lake west of Cold Lake contained concentrations of arsenic that exceeded 25 μg As/L. Such high concentrations in shallow wells (less than 35 m deep) appeared unusual based on data from province wide testing programs. Alberta Environment commissioned a study to better understand the hydrogeology of the area and the geochemical characteristics of groundwater in order to elucidate conditions that may account for the observed high levels of arsenic.

The study area is located about 32 km west of Cold Lake and centered in the Beaver Lowlands which contain Crane, Edward, Ethel, Harold, Hilda, and Maloney lakes. The local geology and hydrology were summarized using published information and lithologic and borehole geophysical data from water well logs from Alberta Environment records. Field measurements and water sampling were conducted in January and February 2000 in conjunction with the Alberta Health and Wellness monitoring program.

The geology of the area consists of marine shale bedrock belonging to the Lea Park Formation overlain by the Empress Formation Unit 3, the Muriel Lake Formation, sand within the Bonnyville Formation, Ethel Lake Formation and the Sand River Formation (listed from oldest to youngest, respectively). These formations constitute the aquifers of the study area. Flow in most of these formations is generally from north to south but with upward and downward components to groundwater flow. The shallow wells, which are the focus of this study, occur in the Sand River Formation.

Results of this study showed that there were no systematic arsenic gradients from north to south in the various aquifers for those areas where adequate data was available. In the area of shallow wells in the Sand River Formation with high arsenic levels, groundwater flow is characterized by

lateral, downward and upward components. For these shallow wells, our study showed the following:

- Well casing type does not account for the elevated levels of arsenic
- The arsenic in shallow wells is of local origin and not from underlying aquifers
- Low redox conditions are related to high arsenic concentrations
- Waters high in arsenic are also high in dissolved iron
- Redox values are sufficiently low that secondary iron oxide minerals dissolve, thereby releasing adsorbed arsenic to groundwater

Our study concludes that arsenic in the shallow wells of the study area originates from the dissolution of iron oxides brought about by the low redox conditions in these shallow wells. The cause of the low redox conditions was not identified in this study.

1. INTRODUCTION

Early results (February to July of 1999) from the year-long monthly water sampling program conducted by Alberta Health and Wellness (AHW) in an area west of Cold Lake, Alberta, showed that arsenic dissolved in those waters ranged in concentration from less than one to 73 migrograms per litre (µg/L). While concentrations in this range were not unexpected in view of previous surveys conducted in the area (Stanley Associates Engineering Ltd., 1979; Canada-Alberta Environmentally Sustainable Agriculture Agreement, 1987; Imperial Oil Resources and Komex International Ltd., 1998; and Nriagu, J.O., 1998), a number of values (greater than 15 µg/L) occurred in water from wells that are relatively shallow (less than 35 m deep). Previous data and current AHW survey data show that the deeper* wells generally tend to have the higher arsenic levels.

A second notable feature about the elevated arsenic concentrations in shallow water wells was the spatial distribution of the wells. They occur primarily in an area as much as six kilometres (km) south of Crane Lake and within one km south of Hilda Lake (Figure 1).

Additionally, it is well known that arsenic is a naturally occurring element in the glacial deposits and bedrock sediments of the Cold Lake area (Andriashek, 2000). Andriashek found arsenic concentrations in the silt and clay fractions of till, clay, and shale sampled from five auger holes to range from five to 12 mg/kg for clay and till, and 10 to 20 mg/kg for bedrock shale. These values indicate that abundant arsenic is available for dissolution from the naturally occurring rock units of the area, especially the bedrock shale, and to a lesser degree from the till and clay units which are in large part derived from the shale.

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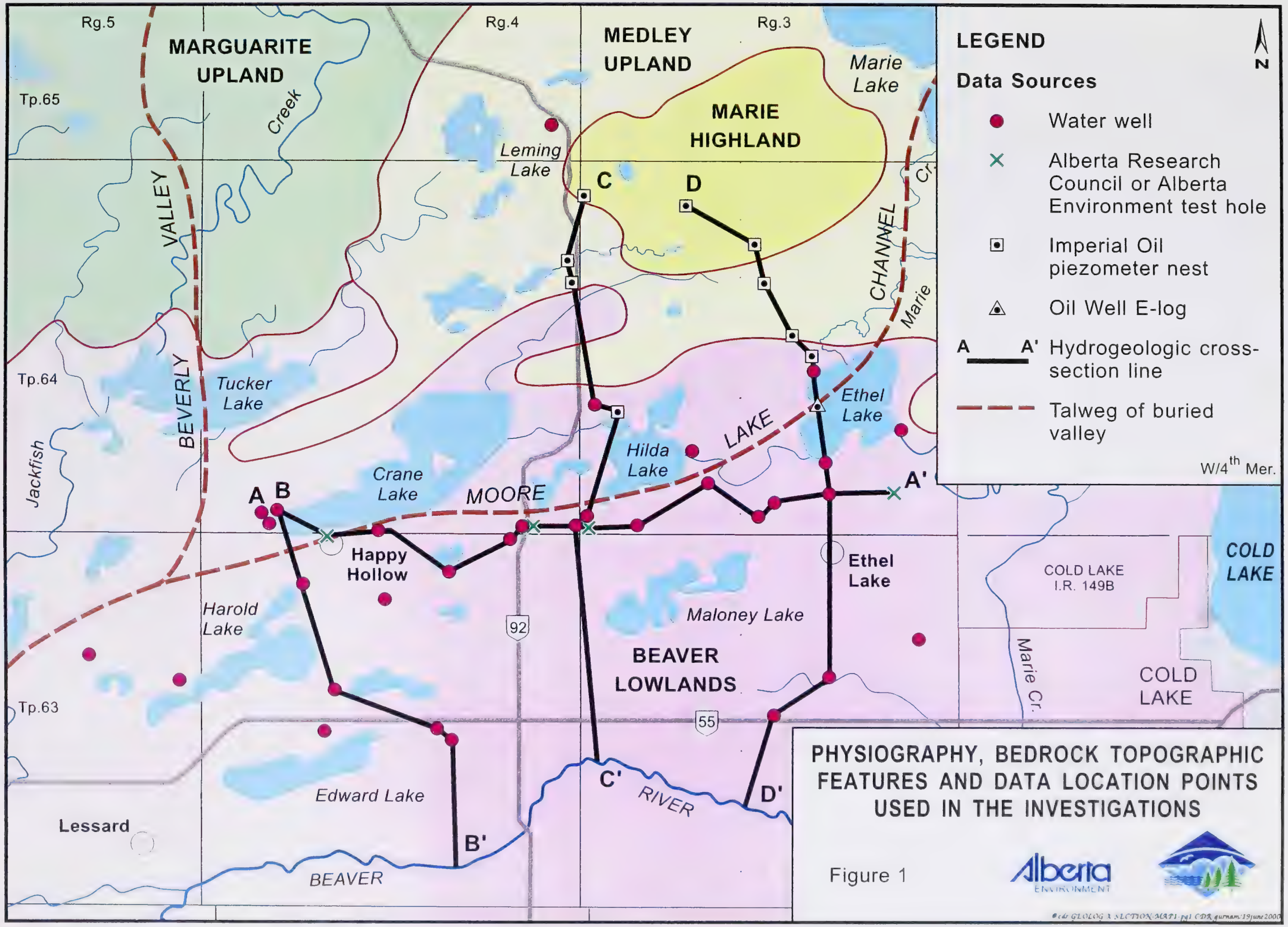
* Throughout this report reference will be made to shallow and deep wells. Shallow wells refers to those completed at a depth of less than 35 m, whereas deep wells are those completed at a depth of more than 35 m.



PHYSIOGRAPHY, BEDROCK TOPOGRAPHIC FEATURES AND DATA LOCATION POINTS USED IN THE INVESTIGATIONS

Figure 1

Although it is well known that arsenic occurs naturally in the local geologic sediments, it was also thought possible that certain anthropogenic causes could manifest in the dissolution of that arsenic and facilitate its presence in the groundwater. For instance, it is possible that introduction of soluble organic matter to groundwater could stimulate microbial activity which in turn would lower the redox potential thereby dissolving and releasing arsenic bound to iron oxides.

Finally, there exists the possibility that arsenic within deep formations is transported from uplands situated in the north part of the study area to the lowlands in the southern part and then discharged upward into shallow aquifers situated beneath the southern lowlands.

In view of the elevated arsenic concentrations in shallow wells, their apparent clustering south of Crane and Hilda lakes, and the possibility for anthropogenic causes, Alberta Environment (AENV) decided to conduct an investigation into the local groundwater conditions to better understand the conditions that could explain the elevated concentrations, especially in shallow wells.

2. DESCRIPTION OF THE STUDY AREA

The area chosen for this investigation consists of all or parts of Townships 63 to 65 and Ranges 3 to 5, west of the Fourth Meridian (Figure 1). The area extends approximately 32 km west of Cold Lake and encompasses a variety of physiographic features.

Topography is dominated by a series of elevated uplands (Marguarite and Medley uplands, and the Marie Highland), rising to as much as 663 m and located in the northern third of the area, and a well defined lowland known as the Beaver Lowlands that occupies the southern two-thirds at an elevation of about 548 m (Andriashshek and Fenton, 1989). The area occupied by the Beaver Lowlands is characterized by a number of lakes (Crane, Hilda, Ethel, Harold, Edward and Maloney lakes) separated by a number of local elevated areas rising as much as 38 m above the lake elevations. Major drainage is provided by the Beaver River in the southern part of the area which drains west to east into Cold Lake, and by Marie Creek draining north to south from Ethel

Lake into the Beaver River in the eastern part. The Beaver River is incised sharply more than 38 m into the Beaver Lowlands.

3. METHODOLOGY AND SAMPLING

The focus of this investigation was primarily to determine the source of the elevated arsenic levels in water from shallow wells less than 35 m deep located south and east of Crane Lake, and in particular, if the elevated arsenic results from natural or anthropogenic processes.

The local geology and hydrogeology were examined from existing information (Andriashek and Fenton, 1989; Imperial Oil Resources and Komex International Ltd., 1998; L.D. Andriashek, Alberta Geological Survey, unpublished information) along with lithologic and borehole geophysical data from water well logs available from AENV records.

Additionally, a field investigation was conducted in January and February of 2000 to provide site-specific information relevant to the physical hydrogeology and hydrochemistry of the area. This investigation was conducted cooperatively and in tandem with the AHW survey and consisted of the following:

1. Physical examination of 36 water well sites participating in the AHW survey to determine if well construction, particularly the use of wooden casing, or other local carbon sources, such as barnyard runoff could be contributing excess organic carbon which could be lowering redox potentials;
2. Sampling of well water for major ion analysis by AHW for January of 2000;
3. Analysis of well water for total organic carbon (TOC);
4. In-situ measurement of pH, Eh, temperature, and dissolved oxygen;
5. Measurement of well elevations and location with a Global Positioning System (GPS) accurate to within most surveying systems; and
6. Determination of non-pumping water levels for all accessible wells.

For this investigation only water that had not undergone any form of treatment, such as iron removal or softening, was sampled. A few wells could not be monitored for water level because the well heads were insulated and the owners did not wish to expose them to low temperatures prevalent in February.

4. RESULTS

4.1 Geology

The geology of the area was previously evaluated by Andriashek and Fenton (1989) and considerable new information has been generated by Imperial Oil and Komex (1998) in the northern part of the area in response to an Environmental Protection Order.

Bedrock of the area consists of shale of the Lea Park Formation. The shale is of Upper Cretaceous age and was deposited in a marine environment. Marine shales often contain pyrite which is known to be enriched in arsenic.

The bedrock surface was modified by Tertiary erosion and is characterized by a series of bedrock uplands into which a number of drainage valleys, originating from the Rocky Mountains, are carved. Two such valleys, the Beverly Valley extending to the north in the western part of the area (Figure 1) and Helina Valley, which runs west to east and is located a few kilometres north of the study area are important to the hydrogeology of the area. The valleys are incised as much as 65 m into the bedrock surface and are floored by sand and gravel of the Empress Formation, Unit 1 (Andriashek and Fenton, 1989). A bedrock upland which rises to an elevation of about 510 m extends east of the Beverly Valley, and south of the Helina Valley.

The area experienced at least four glacial advances and retreats that left a thick mantle of glacial, glaciofluvial and glaciolacustrine sediments in the area. The glacial advances and retreats were accompanied by significant amounts of meltwater both beneath the glaciers and at the glacier margins. This fluvial activity resulted in the carving of some glacial channels (the Moore Lake Channel, Figure 1), and is responsible for the deposition of the sequence of aquifers that now

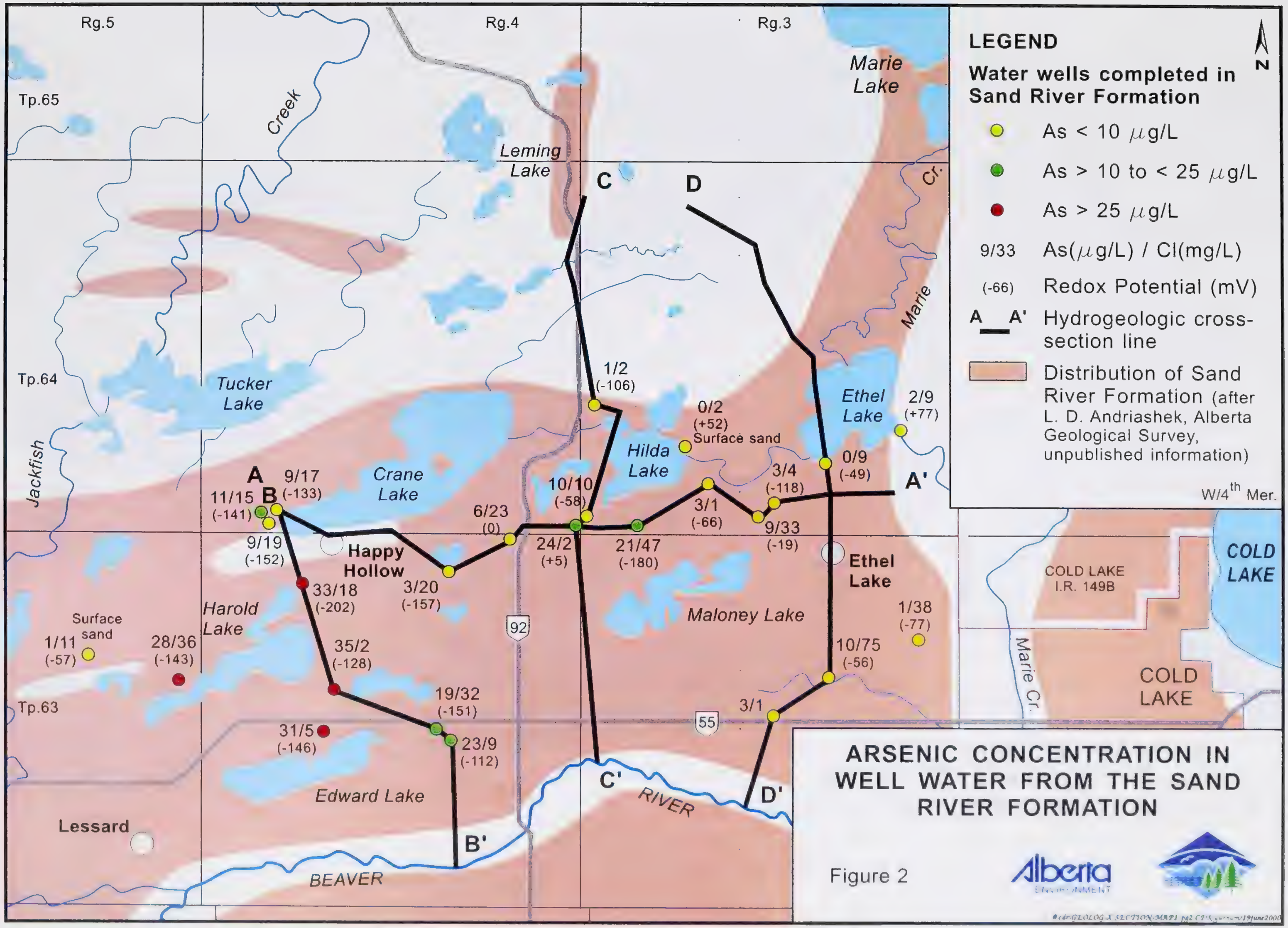
characterizes the area. From oldest to youngest these aquifers are known as the Empress Formation Unit 1, Empress Formation Unit 3, the Muriel Lake Formation, sand within the Bonnyville Formation, Ethel Lake and the Sand River Formation.

The oldest aquifer, the Empress Formation Unit 1, is shown by Imperial Oil and Komex (1998) to exist only in the northern and western part of the area (data not presented) and occupies the lowest parts of Helina and Beverly valleys. The Empress Unit 3 is much more widespread and is present beneath most of the uplands. The formation extends as far south as about 2 km south of Crane, Hilda, and Ethel lakes (Imperial and Komex, 1998; Andriashek, unpublished information). The Muriel Lake Formation is also laterally extensive over the study area but extends further south to beyond the Beaver River (Andriashek, unpublished information).

Two sand units are present within the Bonnyville Formation and according to Imperial Oil and Komex (1998) they behave hydraulically as one connected unit. The units exist beneath most of the uplands with southward extensions to Ethel and Hilda lakes and toward Tucker and Crane lakes.

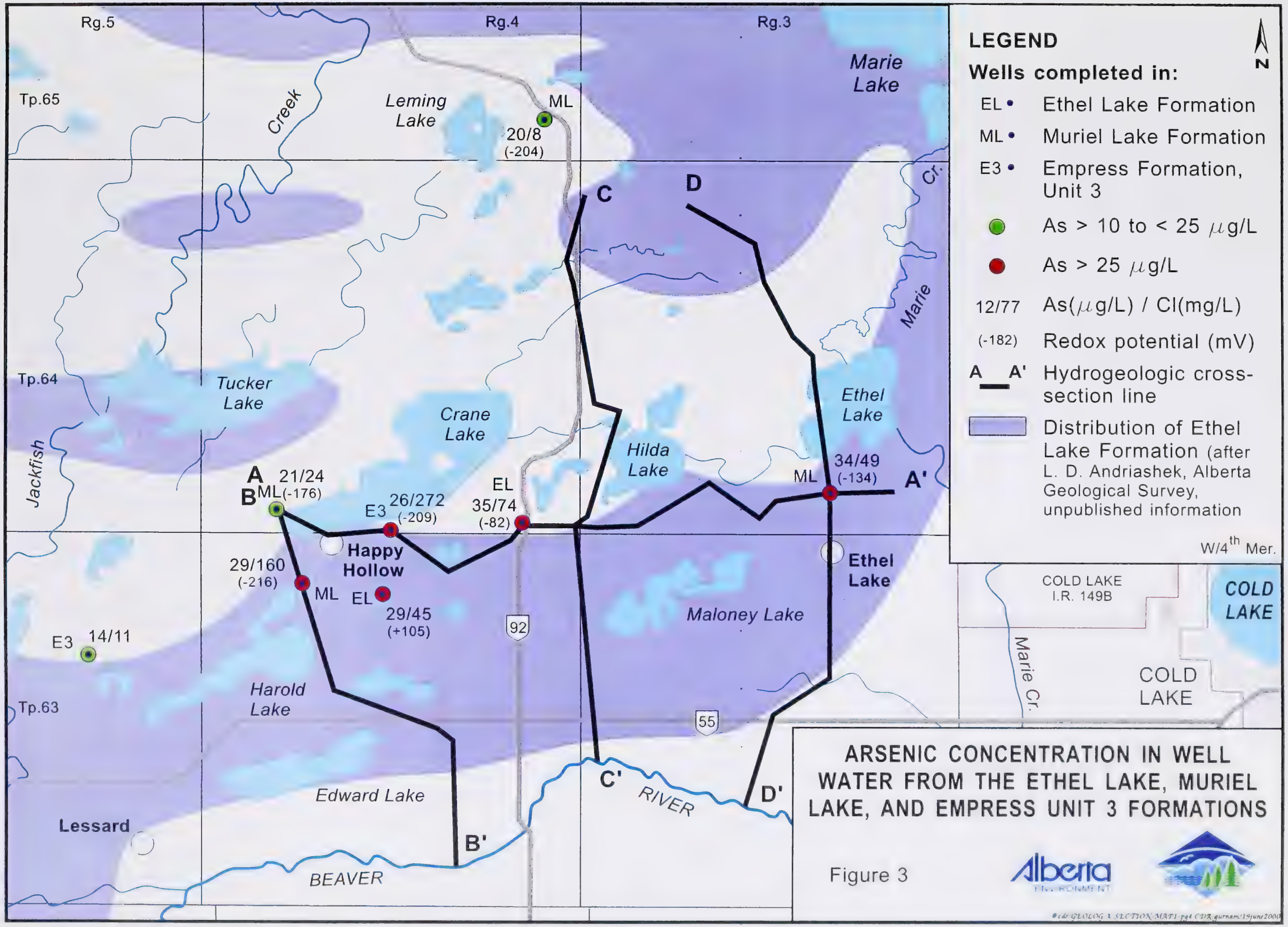
The distribution of the Sand River and Ethel Lake formations is shown in Figures 2 and 3, after L.D. Andriashek (unpublished information). Andriashek's interpretation of the distribution of the Sand River formation is that, with the exception of a few small outliers, it exists essentially beneath the Beaver Lowlands with an extension to the north beneath Ethel and Marie lakes and beneath the Medley Upland. The base of the uplands essentially defines the northern boundary and the Beaver River has cut down through the entire thickness of the formation along its course.

The distribution of the Ethel Lake formation is somewhat similar, in that a large part is found beneath the Beaver Lowlands with an extension to the north beneath Ethel and Marie Lakes (Figure 3). However, the formation is more extensive than the Sand River formation in the north.



ARSENIC CONCENTRATION IN WELL WATER FROM THE SAND RIVER FORMATION

Figure 2



ARSENIC CONCENTRATION IN WELL WATER FROM THE ETHEL LAKE, MURIEL LAKE, AND EMPRESS UNIT 3 FORMATIONS

Figure 3

4.2 Hydrogeology

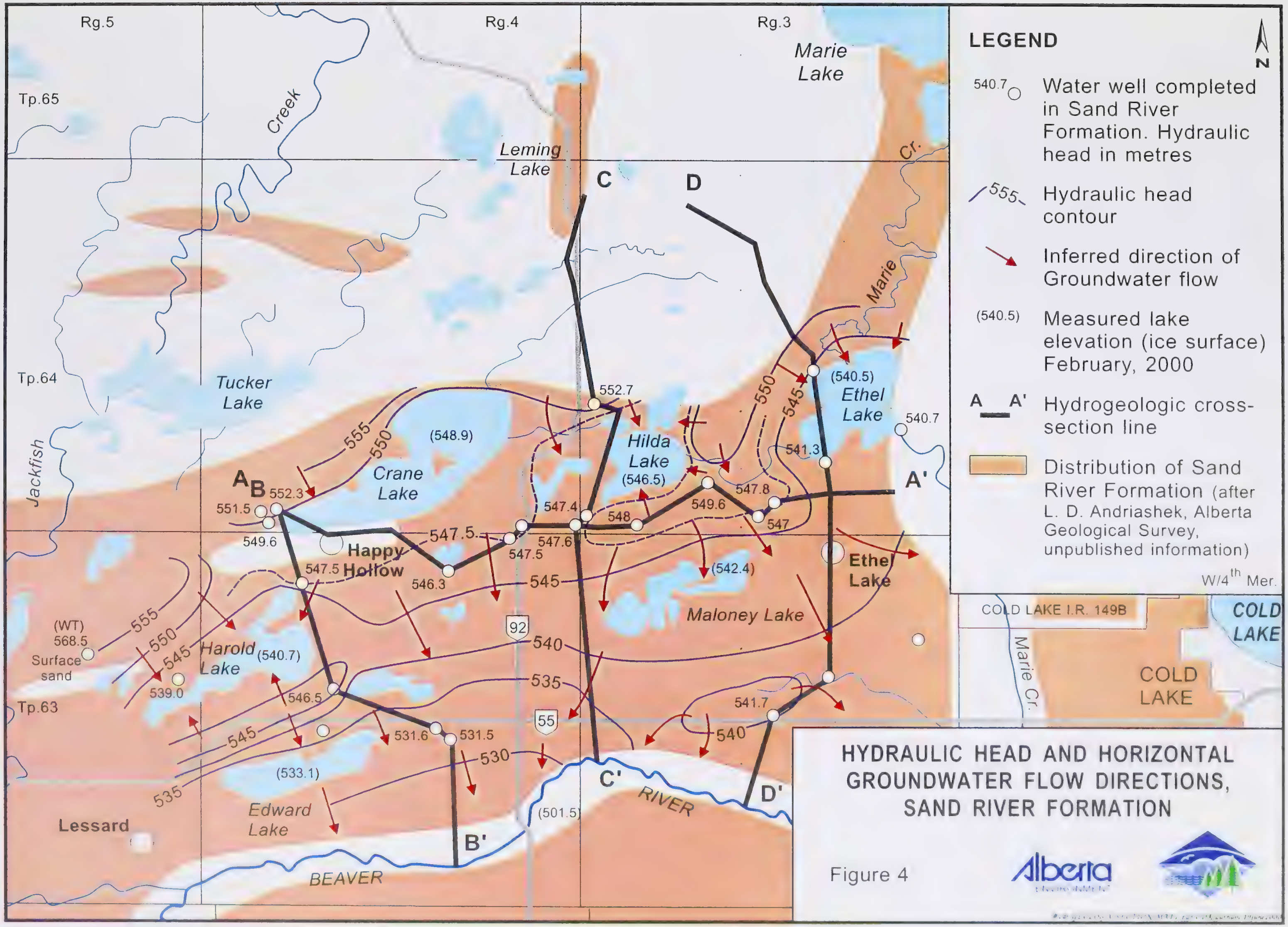
Information about the hydrogeology of the area is derived from Imperial Oil and Komex (1998) and from hydraulic head data gathered during this investigation. Imperial Oil and Komex provide maps showing groundwater flow directions in the Empress Formation Unit 3 and in the Muriel Lake Formation. The highest hydraulic heads in both formations are found essentially beneath the northern uplands and especially beneath the Marie Highland. Groundwater flow essentially radiates outward toward Marie Lake and south toward the Beaver Lowlands. Hydraulic heads in the Muriel Lake Formation are as much as 5 m higher than in the Empress Formation Unit 3, indicating that a downward hydraulic gradient exists beneath the uplands.

This configuration is consistent with the concept that the northern uplands constitute a dominant area for groundwater recharge and that groundwater flow in the deep aquifers is from the upland areas to the lowlands in the south.

Information gathered for this investigation is presented and interpreted in two ways. First, because the prime focus was on elevated arsenic concentrations found in shallow wells, the hydraulic head distribution and inferred groundwater flow directions are presented in map form for areas underlain by the Sand River Formation (Figure 4). Second, a series of cross-sections was constructed to show the distribution of groundwater flow in both the vertical and horizontal directions (Figures 5 to 8).

4.3 Groundwater Flow within the Sand River Formation

The distribution of hydraulic head within the Sand River Formation shows a pattern of elevated heads in northern parts with a steady decrease toward the formation outcrop at the Beaver River valley (Figure 4). Superimposed on this general southward gradient, are local areas of elevated heads beneath locally elevated areas of the Beaver Lowlands, for instance between Hilda and Ethel and Maloney lakes, northwest of Harold Lake and between Harold and Edward lakes. The pattern of groundwater flow derived from these data is that groundwater within the Sand River



HYDRAULIC HEAD AND HORIZONTAL GROUNDWATER FLOW DIRECTIONS, SAND RIVER FORMATION

Figure 4

Formation flows essentially from north to south where it discharges at its outcrop along the Beaver River valley. Local areas of elevated topography constitute areas where local recharge is occurring.

An important aspect about groundwater flow in the Sand River Formation is that, with the exception of its extension between Ethel and Marie lakes, flow from the northern uplands to the Beaver Lowlands cannot occur because the formation does not physically extend to the uplands.

4.4 Groundwater Flow Patterns Derived from Cross-Sections

Hydraulic head values shown on the cross-sections are derived from the February 2000 sampling event in the southern part of the area and from information published in Imperial Oil and Komex (1998) for the northern part. For these sections, the position of the water table could only be crudely estimated, but was generally taken to be 2 to 5 m deep, shallow in low-lying areas and somewhat deeper in upland areas. The error introduced by this uncertainty should not be too great, however, because such water table depths appear reasonable for the type of climate and the generally clayey surface sediments associated with the area.

A complicating factor in the cross-section presentations is that they were constructed with a vertical exaggeration of about 63 times. This exaggeration was needed to show geologic complexity but complicates the derivation of the direction of flow lines from equipotential lines. The directions of hydraulic gradients remain valid however and the major component directions of groundwater flow (that is, up, down, or lateral) are similarly valid.

4.4.1 Cross-Section A-A'

Cross-Section A-A' (Figure 5) extends across the area from west to east. The section was constructed to allow inclusion of many of the water wells but extends perpendicular to the expected major hydraulic gradient of the area, that being from the northern uplands and south

LEGEND

HYDROGEOLOGIC CROSS SECTIONS

🟧	Sand River Formation: Sand and gravelly sand; minor silt and clay
🟦	Ethel Lake Formation: Silt and clay, minor sand, gravel and diamicton
🟩	Sand within Bonnyville Formation
🟥	Muriel Lake Formation: Sand and gravel, minor silt and clay
🟪	Empress Formation Unit 3: Sand and gravel; contains igneous and metamorphic clasts derived from the Canadian Shield
▨	Thrust shale derived form the Lea Park Formation
☐	Lea Park Formation: Shale
• 552.3	Measured hydraulic head, metres above sea level
▼	Estimated position of the Water Table
-555-	Equipotential Line, hydraulic head, metres above sea level
⇙	Inferred direction of groundwater flow

Arsenic concentration: Average, in μg/L, of all Alberta Health determinations, Feb. 1999 to Feb. 2000 and Imperial Oil determinations, various dates September 1996 to June 1998

🟡	As < 10 μg/L
🟢	As > 10 to < 25 μg/L
🔴	As > 25 μg/L
35/74	As(μg/L) / Cl(mg/L)
(-134)	Redox Potential (mV)

WATER
WELL

WATER
WELL
Lithology
not available

ARC

ALBERTA
RESEARCH
COUNCIL
TEST HOLE

GEW 97-2

IMPERIAL OIL
PIEZOMETER
NEST

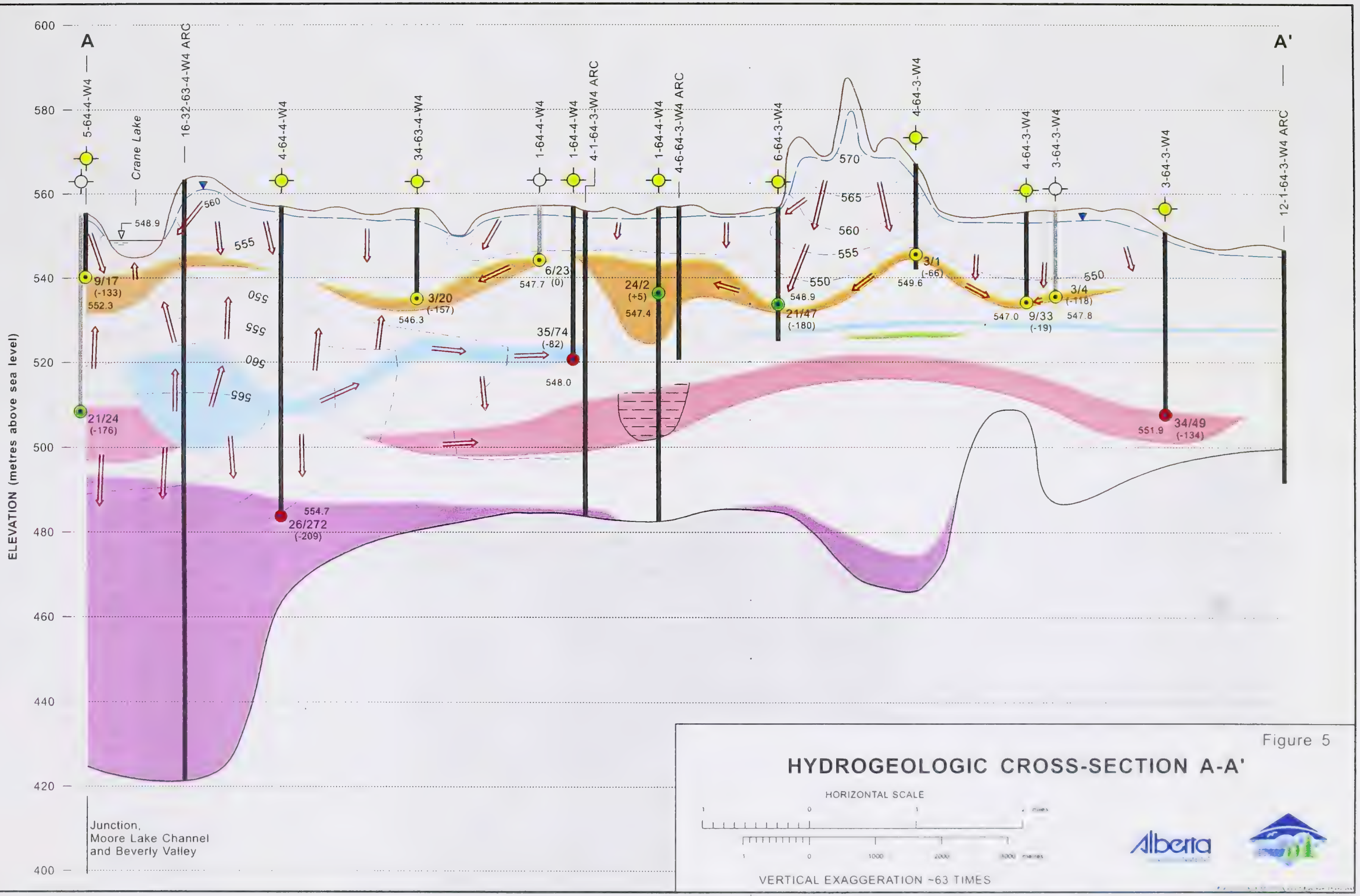


Figure 5

HYDROGEOLOGIC CROSS-SECTION A-A'

toward the Beaver River. Much of the groundwater flow is thus out of the section and toward the reader, however, vertical gradients and components of flow are valid.

The cross-section depicts several important features of the inferred groundwater flow configuration of the area. First, except for directly below Crane Lake at the west end of the section, all flow between the water table and the Sand River Formation is downward, toward the Sand River Formation. That is, the formation receives recharge from above over almost the entire length. Particularly strong downward gradients are generated beneath the local elevated area near the eastern part of the section.

Second, high hydraulic heads are found in deeper aquifers (Empress Unit 3, Muriel Lake and Ethel Lake formations) along the western third of the section. The deep well completed in the Muriel Lake Formation at the west end of the section is a flowing well and the head could not be measured. A well completed in the same formation and located about 1.5 km south of this location has a hydraulic head of 566.6 m and extrapolating this information to Section A-A' requires very high hydraulic heads within the Muriel Lake Formation. The conclusion that may be drawn from this situation is that the Muriel Lake Formation provides a ready avenue for the transmittal of high hydraulic heads from the northern uplands to the Crane Lake area. Because the Ethel Lake Formation has incised the Muriel Lake Formation in this area, high heads are also transmitted along the former unit.

A second conclusion that may be drawn from the hydraulic head configuration is that, in the western half of the section, the upward flow from the Muriel Lake and Ethel Lake formations to the Sand River Formation, may be as great or greater than the downward flow from above. This derives from the relative magnitudes of the upward and downward hydraulic gradients. Beneath the local upland just east of Crane Lake, upward and downward gradients are about equal. Farther east (for about 3 to 4 km), the upward gradient is greater than the downward gradient. If the hydraulic conductivity of till units above and below the Sand River Formation is similar, this would imply that the upward flux of groundwater to the Sand River Formation is as great or greater than the downward flux.

A strong cautionary note must be applied here because the hydraulic heads in the Muriel Lake and Ethel Lake formations are not measured in this area, but are extrapolated from about 1.5 km away. The hydraulic heads and magnitude of the upward gradient could thus be lower than shown and concomitantly the upward groundwater flux would also be lower.

Thus, along the western part of Section A-A' the Sand River Formation receives local recharge from above, and also receives groundwater from the Muriel Lake and Ethel Lake formations from below. Not enough head information is available in the eastern half of the section to evaluate flow in aquifers lower than the Sand River Formation.

4.4.2 Cross-Section B-B'

Cross-Section B-B' (Figure 6), extends approximately north to south from the western end of Crane Lake to the Beaver River. The section was constructed parallel to the anticipated regional hydraulic gradients and both vertical and horizontal groundwater flow directions can be inferred. The section extends through a number of wells with elevated arsenic concentrations that are completed in the Sand River Formation.

The hydraulic head and groundwater flow configurations show many similarities to those found on Section A-A'. Again, almost the entire line of section B-B' shows that recharge from the surface and downward flow into the Sand River Formation dominates the upper part of the section. The influence of local elevated areas on providing local recharge to the Sand River Formation is clearly apparent.

Two wells completed in the Muriel Lake Formation at the north end of the section again clearly show the very high hydraulic head within that Formation. Along about the northern half of the section flow is upward from the Muriel Lake to the Sand River Formation. In this area, therefore, the Sand River Formation receives both recharge from above and flow from the Muriel Lake Formation below. The relative amounts of these influxes can again be estimated from the relative magnitudes of the gradients above and below the Sand River Formation. Beneath the two local uplands along the north half of the sections, upward and downward

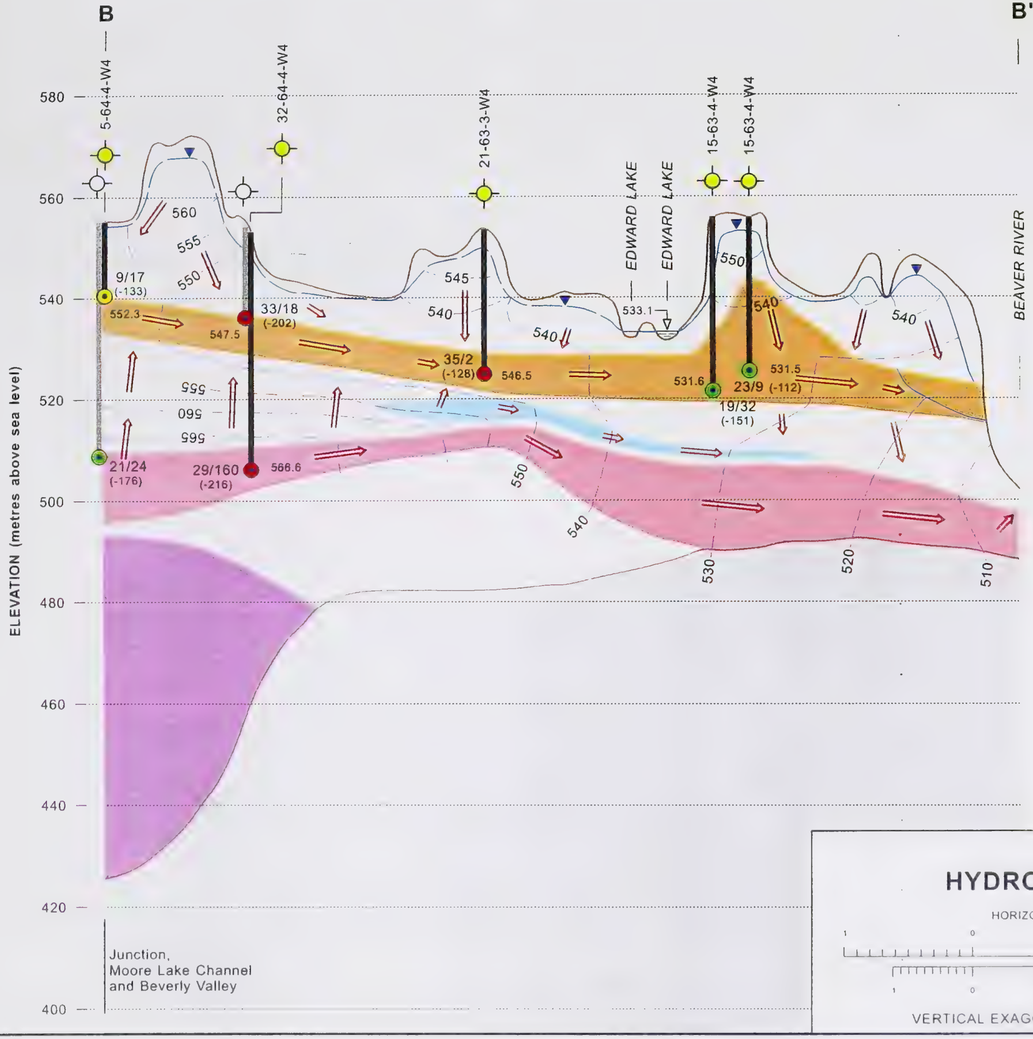


Figure 6

HYDROGEOLOGIC CROSS-SECTION B-B'

HORIZONTAL SCALE

VERTICAL EXAGGERATION ~63 TIMES

gradients are about equal, implying about equal amounts of recharge from above and below to the Sand River Formation in these areas. Between the local uplands the vertical gradient from below is significantly greater, implying a greater influx from below than above. In fact, this part of the section skirts the east end of Harold Lake and flow from the Sand River Formation may even be directed upward toward the lake bottom. More data are needed to better define this situation. The relative gradients do, however, imply that as much, or more, groundwater flows to the Sand River Formation from below than from above in this part of the section.

It should be noted that the upward and downward fluxes to the Sand River Formation do not constitute all of the water in the formation. In fact, there must be three components that constitute the source of porewater at any one location in the aquifer: vertical upward, vertical downward, and lateral fluxes. Without knowing the quantitative magnitudes of all three fluxes, it is not possible to predict if a particular dissolved chemical parameter, such as arsenic or chloride should increase or decrease by simple mixing of water derived from the three sources.

It is for this reason, for instance, that the relative chloride concentration found in the deep (160 mg/L) and shallow well (18 mg/L), located at 32-64-4-W4 can not be used to infer that the water in the Sand River Formation is made up of 10 percent of water from the deep aquifer. In fact, the most probable answer is that the horizontal flux is the greatest of the three. This last interpretation is supported by the close similarity of water in wells completed in the Sand River Formation at 5-64-4-W4 and 32-64-4-W4 at the north end of the section.

The mixed water in the Sand River Formation moves from north to south and in doing so receives ever greater proportions of recharge from above. Data are not available for the Muriel Lake Formation for the southern two-thirds of the section, but because the Muriel Lake Formation extends vertically to within a few metres of the Beaver River, approximate heads in the southern part can be inferred from that condition. These imply that all water within the Muriel Lake Formation discharges beneath the Beaver River and that within 4 km of the river, flow may be downward from the Sand River to the Muriel Lake Formation.

4.4.3 Cross-Section C-C'

Cross-Section C-C' (Figure 7) extends north to south from the western edge of the Marie Highland to the Beaver River. As would be expected, the dominant flow direction is from the upland toward The Beaver Lowlands and the Beaver River. This appears to be the situation for flow in all aquifers except the Empress Unit 3 aquifer within the Moore Channel. The direction of flow within that unit is likely perpendicular to the cross-section although the limited data do not allow interpretation as to which direction (east or west) that flow is in. The Sand River Formation extends along the southern two-thirds of the section and is again characterized by recharging conditions from above along almost its entire extent. Although hydraulic head data are not available for aquifers below the Sand River Formation along the southern half of the section, it appears unlikely that contribution of water from deeper aquifers to the Sand River Formation is possible. A possible exception is at 1-64-4-W4 where the geologic interpretation of the absence of the Ethel Lake Formation is somewhat tenuous. That is, it is possible that at this location the Ethel Lake Formation extends across to the bottom of the Beaver River Formation. However, Andriashek's unpublished information indicates that the Ethel Lake Formation is absent in this area.

4.4.4 Cross-Section D-D'

Cross-Section D-D' (Figure 8), extends north to south from the Marie Upland, through Ethel Lake and to the Sand River. Part of this section, namely that located between boreholes at 11-28-64-3-W4 and 2-15-64-3-W4, follows part of a cross-section presented by Imperial Oil and Komex, 1998 (their Cross-Section C-C'). The interpretation given here differs slightly from their cross-section presentation. The difference involves interpretation of the continuity of the Bonnyville Formation Sand unit at the Pustanyk water well site and between GEW97-7 and REG96-5. Imperial Oil and Komex (1998) chose to insert discontinuities at these locations, presumably based in part on the lithologic log prepared by the driller of the Pustanyk well.

In fact, there are lithologic logs for two wells available for that location, a deeper (66 m) well with lithology as indicated by Imperial Oil and Komex, and a shallower (28 m) well which indicates at least 14 m of sand exists at the location of the shallow well. The latter well did not

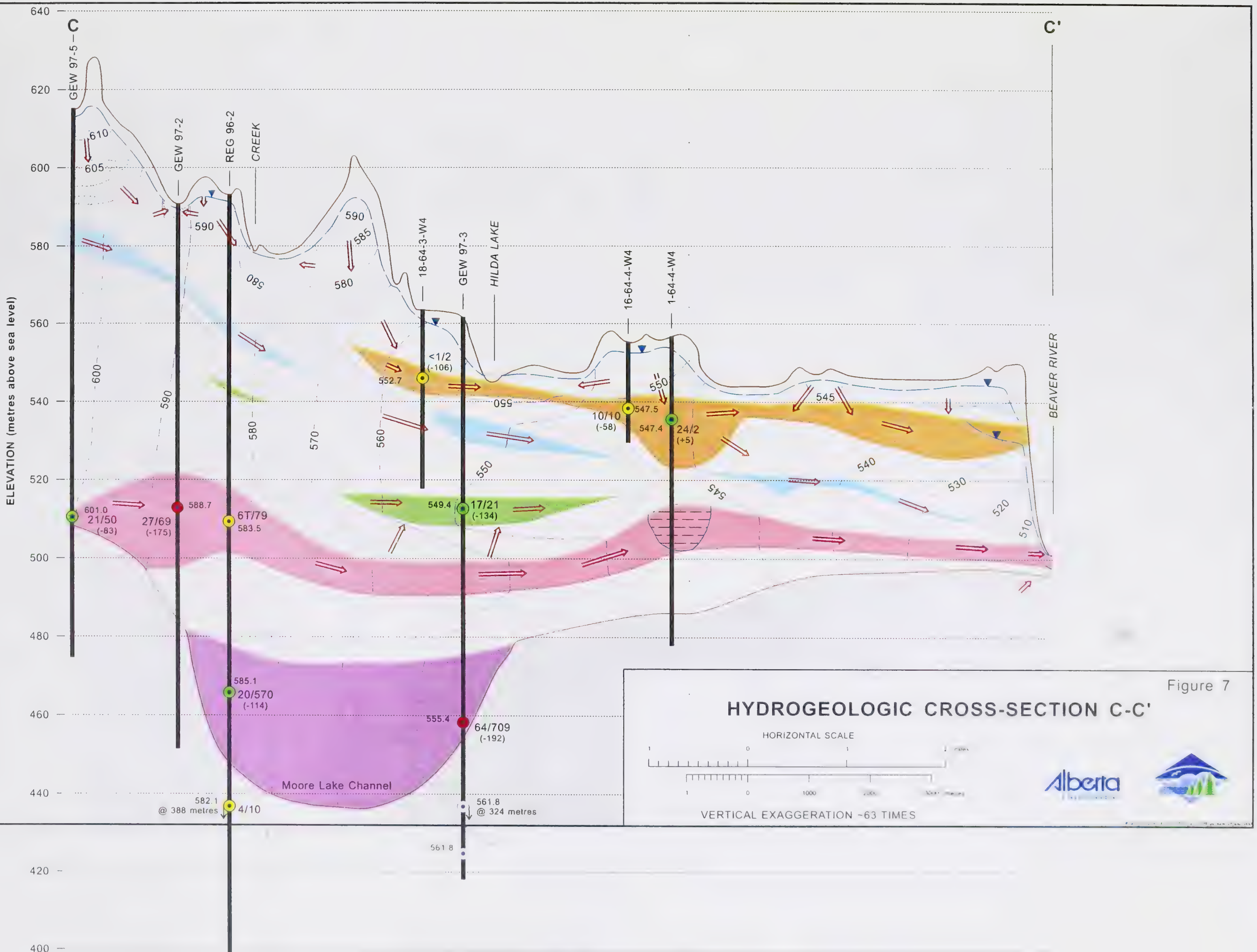


Figure 7

HYDROGEOLOGIC CROSS-SECTION C-C'

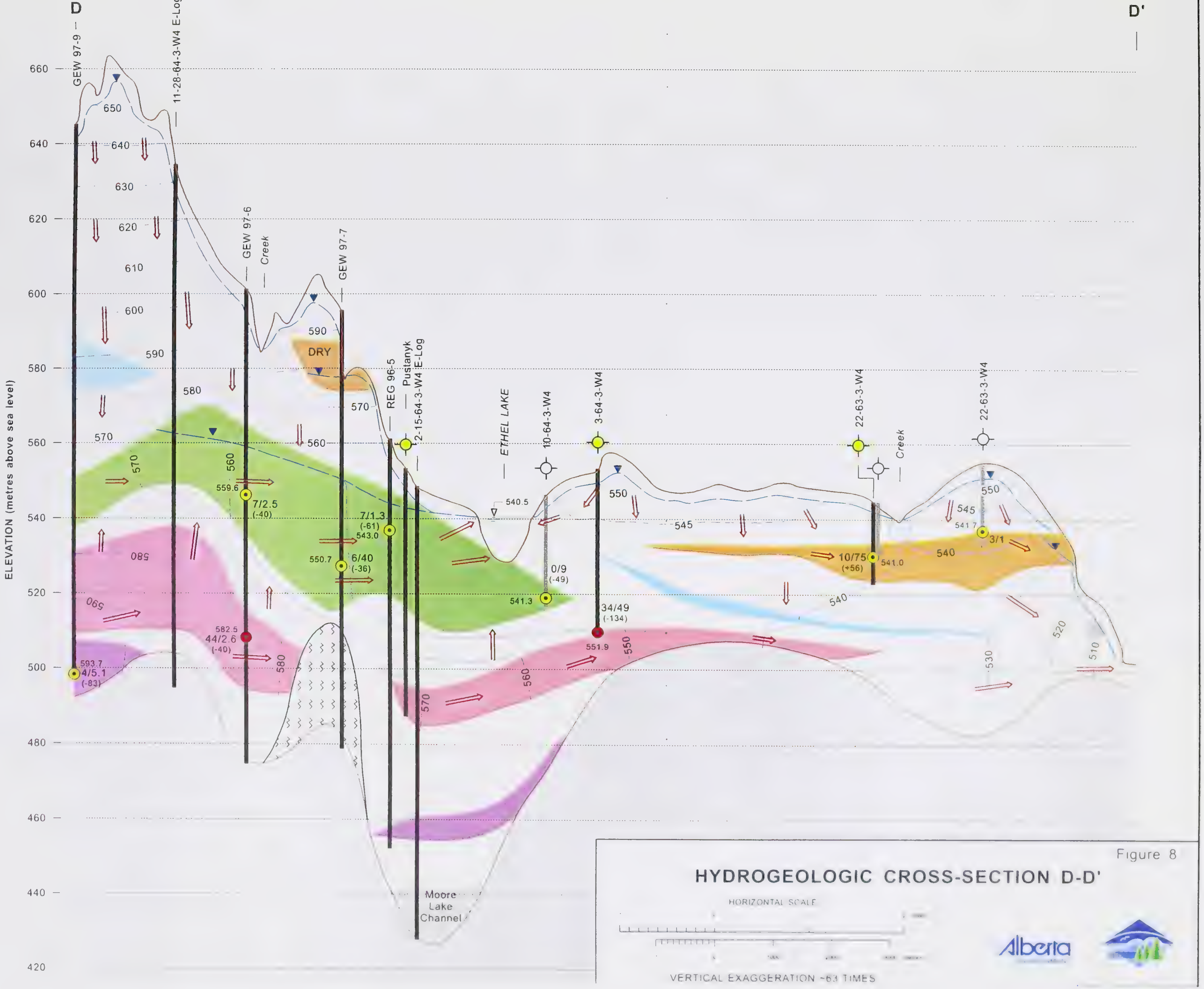


Figure 8

HYDROGEOLOGIC CROSS-SECTION D-D'

penetrate through the sand. The presence of this sand and the remarkably consistent water levels in the Bonnyville sand unit north of Ethel Lake, which would indicate hydraulic continuity within the sand unit, prompted us to opt for the interpretation given here.

A further complicating factor is that the distribution of the Sand River Formation as shown on Section D-D' does not agree with that shown on maps (Figures 2 and 4), presented previously in this report (after Andriashek, unpublished information). Andriashek interpreted that an extremely deep meltwater channel incised to an elevation of less than 470 m containing as much as 64 m of Sand River Formation sediment, was located from the south end of Marie Lake to about 1.5 km south of Ethel Lake and that the formation extends west as far as GEW97-7. The interpretive ambiguity between several investigations is likely caused by high geologic complexity in this part of the area and means that all interpretations should be treated with caution. It should be noted that the water well located south of Ethel Lake (10-64-3-W4) was grouped with data for the Sand River Formation elsewhere in this report, but on Section D-D' it is interpreted to be completed in Bonnyville sand.

In spite of the geological ambiguities, the hydraulic information on the cross-section presents an extremely informative picture. A dominant feature shown on the section is the extensive and thick Bonnyville Formation sand. The Bonnyville sand unit extends from beneath Ethel Lake to the Marie Upland. It appears to be in direct hydraulic contact with Ethel Lake and drains the entire upland toward the lake and the Beaver Lowlands. Furthermore, it is partially drained and contains its own water table, indicating that water can drain from the unit at a faster rate than it can be replenished from above and below. Groundwater flow within the Bonnyville sand is horizontal.

Above the Bonnyville sand, the hydraulic gradient is steep (from about 0.9 to unity) and all groundwater flow is vertical and directed downward. Below the unit flow is directed upward from the Empress Formation Unit 3 and the Muriel Lake Formation. High hydraulic heads in the Empress Formation Unit 3 and the Muriel Lake Formation likely mean that the major recharge for these aquifers extends significantly farther north and west beyond the north end of the section. Groundwater flow beneath the Beaver Lowlands is again directed downward toward the

Sand River Formation, then laterally toward its outcrop along the Beaver River. Limited data for the Muriel Lake Formation indicate that flow is also directed laterally toward the river below the Beaver Lowlands.

4.5 Occurrence of Arsenic within the Groundwater Flow Regime

The following discussion will consider information collected explicitly for this study, and published data available from Imperial Oil and Komex (1998), for those wells and piezometers used in constructing the hydrogeological cross-sections. The locations of these data are shown in Figure 1, and on the cross-sections, Figures 5 through 8. In addition, three wells located within 15 km of the study area were sampled during the January 1999 sampling event and field chemical parameters were measured. These wells cannot be shown on the maps or cross-sections but were used in the general analyses of arsenic versus other parameters in later sections of this report. Two are completed within the Muriel Lake Formation and one within the Ethel Lake Formation. All are positioned above the buried Helina Valley.

One well is located (in 21-65-2-W4) on the northeast shore of Marie Lake and groundwater flow is to the east, from Marie Lake to Cold Lake and away from the study area at that location (Basin Analysis Group, 1985). The other two are located about 10 and 15 km west of the study area in 10 and 18-64-6-W4, respectively. The latter two wells are located at the junction of the Marguarite Upland and Beaver Lowlands. The direction of groundwater flow is not known at these locations but, based on topographic considerations, is thought to be to the southwest, away from the uplands.

Values of arsenic shown on the maps and cross-sections are arithmetic averages of data that were considered acceptable by AHW and were collected during the period of February 1999 to February 2000. Samples for this collection program were not filtered prior to acidizing. Data from Imperial Oil and Komex (1998), are from samples collected during the period from May 1997 to June 1998. With the exception of one sample from the Muriel Lake Formation at Site 96-2 (cross-section C-C') all Imperial Oil samples were filtered before acidizing.

The pattern that emerges is as follows. First, all wells sampled specifically for this study and located within the map area shown in Figures 1 through 4, and which draw their water from formations that are deeper than the Sand River Formation contain elevated levels of dissolved arsenic (Figure 3). These include the Ethel Lake Formation (2 wells), the Muriel Lake Formation (4 wells), and the Empress Formation Unit 3 (2 wells).

Average values for samples collected within the map area by AHW from the Ethel Lake Formation are 29 and 35 μg/L, for the Muriel Lake Formation the values range from 21 to 43 μg/L and for the Empress Formation Unit 3 they are 14 and 26 μg/L (Figure 3). Additionally, for the three wells located outside the study area, arsenic concentrations were 21 μg/L in water from the Ethel Lake well, and 7 (near Marie Lake) and 43 μg/L for water from wells completed in the Muriel Lake Formation.

Values from Imperial Oil and Komex (1998), from the Muriel Lake Formation used on Cross-Sections C-C' and D-D' range from 21 to 44 μg/L (five values, with one exceptionally low value of 6 μg/L). Those from the Empress Formation Unit 3, range from 20 to 64 μg/L (three values, with one exceptionally low value of 4 μg/L).

The Bonnyville Formation sand unit appears to represent a special case that deviates from this basic pattern. Four values presented on Cross-Section D-D' range from 0 to 7 μg/L, whereas one value available for Cross-Section C-C' is 17 μg/L. The difference between arsenic levels in the Bonnyville sand unit of the two cross-sections can most likely be attributed to hydraulic characteristics. The Bonnyville sand unit on Cross-Section D-D' is unsaturated in its uppermost part, whereas that of Section C-C' is fully saturated. It is significant that along Cross-Section D-D' the low arsenic values within the Bonnyville Formation sand unit remain low, even though water with a high arsenic concentration in the underlying Muriel Lake Formation (44 μg/L) flows upward and into the Bonnyville sand unit. As before, we interpret this to indicate that the lateral, southward groundwater flux through the Bonnyville sand by far exceeds the vertical flux from the underlying Muriel Lake Formation.

Second, water from wells completed in the Sand River Formation generally contains low concentrations of arsenic in the study area, but one cluster of six wells located as much as six km south of Crane Lake, and two wells located about one km south of Hilda Lake contain values ranging from 19 to 35 μg/L (Figure 2).

Groundwater flow patterns derived on Cross-Section B-B' and in Figure 3 indicate that, whereas recharge to the Sand River Formation from above occurs over almost all of the area underlain by the formation, upward flow from the Muriel Lake and Ethel Lake formations (and probably originating from the major uplands to the north), occurs as far as 5 km south of Crane Lake (Figure 6, Cross-Section B-B'). However, relative concentrations of chlorides in the Sand River and Muriel Lake formations south of Crane Lake show that the contribution from below could not constitute more than about 10 percent of the water flowing within the Sand River Formation. As water in the Sand River Formation moves south toward the Beaver River the proportion of locally recharged water from above should increase even more over that derived from below. Thus, the groundwater flow patterns along with relative chloride concentrations appear to indicate that the major source for dissolved arsenic in the Sand River Formation south of Crane Lake is local, and must be derived from local geologic material.

The two Sand River wells with elevated arsenic located south of Hilda Lake are somewhat more difficult to explain. Both wells appear on Cross-Section A-A' and one on C-C'. The geologic interpretation presented on the sections is based largely on a borehole geophysical log available at 1-64-4-W4. The log indicates that an approximately 20-m thick fluvial sequence of probably clayey silt and sand exits at this location.

The geologic interpretation is tenuous at this location, and it is possible that the sediments of the Ethel Lake Formation have been incised by the Sand River Formation, thus creating hydraulic continuity between the two. If this were the case, some of the dissolved arsenic in the Sand River Formation could be derived from the Ethel Lake Formation. However, the local upland south of Hilda Lake does constitute a significant recharge area and would appear to exert a major influence on the source of water to the Sand River Formation. Therefore, the situation cannot be resolved with the data available to date.

Sand River wells elsewhere in the Beaver Lowlands have average dissolved arsenic concentrations of less than 10 µg/L. These are all located in areas where recharge to the Sand River Formation is dominantly from above and hydraulic gradients below the formation are either horizontal or downward.

4.6 Arsenic Gradients within Formations Extending From the Northern Uplands to the Beaver Lowlands

Differences in arsenic concentrations between the northern uplands and the Beaver Lowlands can only be discussed for wells and piezometers completed within the Bonnyville Formation Sand Unit, the Muriel Lake Formation, and the Empress Formation Unit 3. This limitation arises because, with the exception of one well, located in 18-64-3-W4, no arsenic values are available for water from the Sand River or Ethel Lake Formations along the two lines of Cross-Section C-C' and D-D', (Figures 7 and 8) that extend from the uplands to the lowlands.

As discussed in the previous section, arsenic concentrations in piezometers completed in Bonnyville Formation sand are very low (<10 µg/L) in those parts which are only partly saturated. One value, on the other hand, available where the formation is fully saturated is 17 µg/L.

Arsenic values found in Muriel Lake water range from 6 to 44 µg/L (5 values) beneath the uplands and do not appear to be significantly different from those in the lowlands which range from 21 to 43 µg/L (6 wells) with one value of 7 µg/L (at the northeast shore of Muriel Lake). Arsenic values for the one distant well to the west is included in the latter range.

Values for three piezometers completed in the Empress Formation Unit 3 beneath the uplands are 4, 20 and 64 µg/L. Those for two wells beneath the lowlands are 14 and 26 µg/L. Again, no difference appears to exist beneath the uplands and lowlands.

While it is conceded that the number of samples available for this comparison is low, the data do indicate that there is no pattern in the arsenic concentrations that would indicate a greater concentration in the uplands than in the lowlands. No discernible difference is apparent.

4.7 Geochemistry of Groundwater

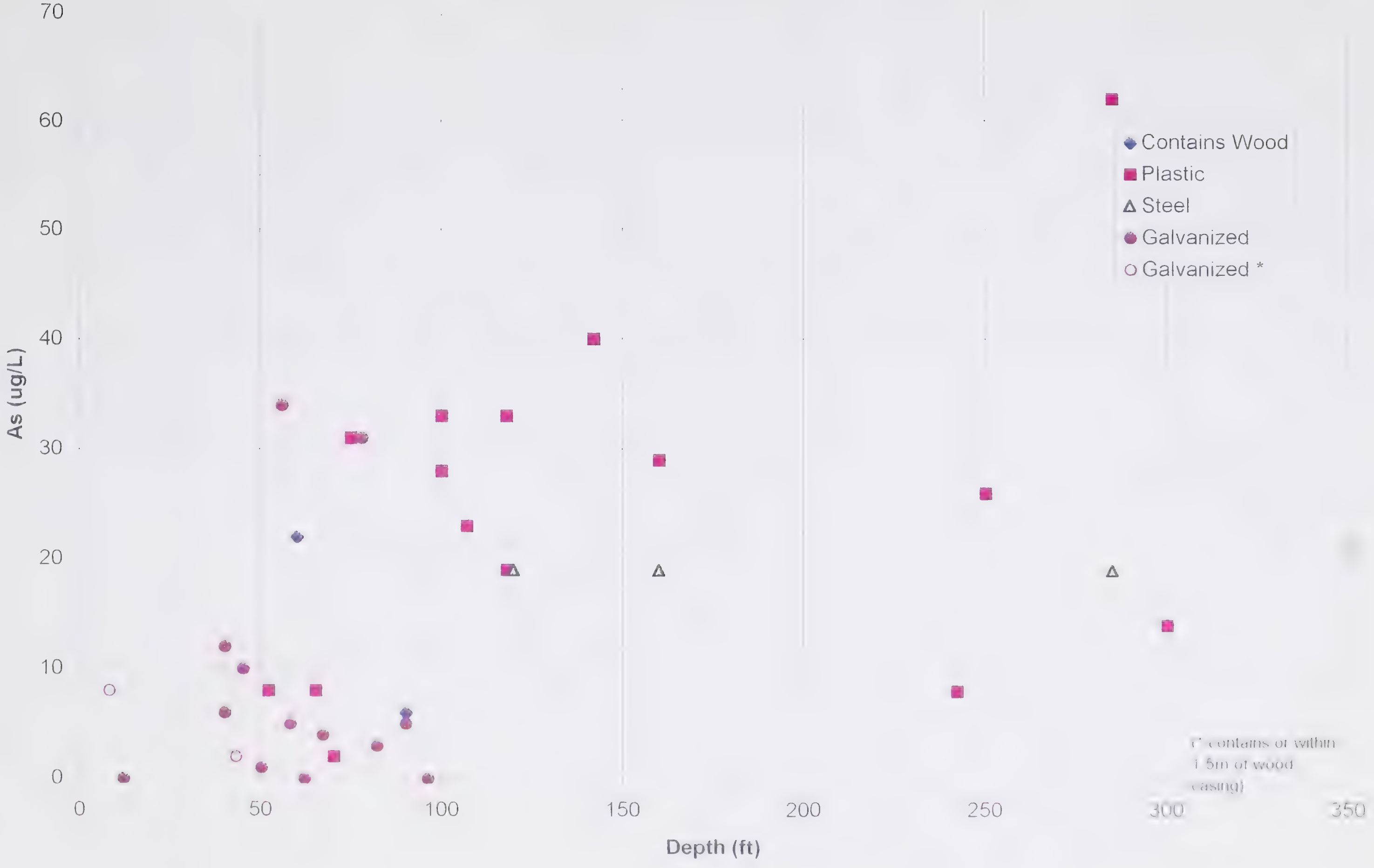
A number of geochemical and well construction parameters were examined in order to better understand the basis for the arsenic concentrations in the study area. The high concentrations of arsenic in shallow wells were of particular interest. Several hypotheses could be advanced to account for these high concentrations. These hypotheses focus on processes that contribute to the geochemical mobilization of native arsenic by reduction of iron oxides.

4.7.1 Arsenic, Well Depth and Casing Type

One possible cause of elevated levels of arsenic in shallow wells of the study area could be due the kind of material used for well casing. In particular, it was thought that the use of wood casing could contribute to well-water levels of arsenic by rotting of wood and its indirect affect on lowering of the redox potential. A lowering of the redox potential could bring a reduction in iron oxides and facilitate the release of adsorbed arsenic.

The results for the comparison of January arsenic concentrations for different well construction materials and depth are shown in Figure 9. The most obvious feature from the data is the general relationship of increasing arsenic levels with well depth, which agrees with the results of the AHW survey outlined in the first section of this report (Alberta Health and Wellness, 2000). Plastic casings were the most commonly used well construction material. Plastic casings occur in wells with the lowest and highest arsenic values encountered in this study. The cluster of arsenic values seen in the area of 20 to 40 μg/L by 50 to 150 ft depth contains all four construction materials.

Figure 9
January Arsenic vs. Depth by Casing Type



Only two of the shallow wells were constructed with wooden casing. However, two others were constructed either within, or in close proximity to (within 1.5 m), old collapsed and rotted wood casings. These are also shown separately in Figure 9. There is no overall higher arsenic concentration apparent for water from the four wells completed with, or in close proximity to, wooden casings. One has a high value of 33.4 µg/L, whereas the other three range from 1 to 9.2 µg/L. While it is conceded that the sample population is too small to allow a definitive conclusion, this study finds that there does not appear to be a relationship between high arsenic concentrations and the use of wooden well-construction material among the four such wells that were sampled.

4.7.2 Chloride and Well Depth

Chloride concentrations are a useful indicator of hydrogeological processes and anthropogenic activities that could relate to elevated arsenic in the shallow wells of the study area. High chloride concentrations are associated with water of deep aquifers and bedrock of marine origin. Deep aquifers also have low redox potentials and can have higher than desirable levels of arsenic. If the shallow wells of this study were significantly impacted by deeper groundwater, one would expect to see elevated concentrations of chlorides in shallow wells. However, all of the hydrogeological data presented earlier in this report indicates the shallow wells of this study are not significantly influenced by flow from the deeper aquifers.

A second source of chloride ions is from barnyard runoff. Runoff from manure storage and livestock corral areas is well known to contain high concentrations of chloride, so the ion also serves as a tracer or indicator of animal waste contamination. If such runoff was impacting shallow wells, the high levels of dissolved organic compounds could be a factor in elevated arsenic concentrations. The connection is that dissolved organic compounds serve as an energy source for microbial activity. A surge in microbial activity stimulated by a source of organic carbon could result in a drop in the redox potential which then could cause a release of iron oxide bound arsenic (discussed in detail in section 4.7.5).

The results for chloride and well depth are shown in Figure 10. All of the shallow wells contain low levels of chlorides. Except for two wells screened in the Muriel Lake Formation, all wells tested contained levels of chloride commonly found in surface soils and shallow groundwater throughout Alberta.

4.7.3 Chloride and Total Organic Carbon (TOC)

Total organic carbon in well water samples is essentially a measure of dissolved organic compounds. Nearly all groundwater will contain some dissolved organic material. Both native and anthropogenic sources are possible in groundwater. In the case of the shallow wells of this study, TOC ranges from about 3 mg/L to 14 mg/L (Figure 11). There is no apparent correlation of TOC with chloride concentrations. This indicates the TOC in the shallow wells is likely derived from natural sources (soil organic matter) and not from run-off and recharge from livestock rearing areas. Values of 6 to 10 mg/L are not unusual for TOC in groundwater.

4.7.4 Arsenic and Total Organic Carbon (TOC)

The relationship between arsenic in groundwater and total organic carbon was examined because of the possible consequences of TOC on redox potential. A high concentration of TOC could drive the redox potential down which in turn could cause the dissolution of iron oxides and release of adsorbed arsenic (discussed in section 4.7.5).

Figure 12 shows there is no systematic relationship between TOC and arsenic concentrations. Shallow wells screened in the Sand River Formation generally contain 5 to 11 mg TOC/L for low through high arsenic concentrations. The four shallow wells with highest TOC have from near 0 to about 21 μg As/L. It is conceded that the presence or absence of TOC is not necessarily a good indicator of redox conditions. For example, very low levels of TOC could be associated with high or low redox conditions, the former if organic substances were always

Figure 10
Chloride vs. Well Depth

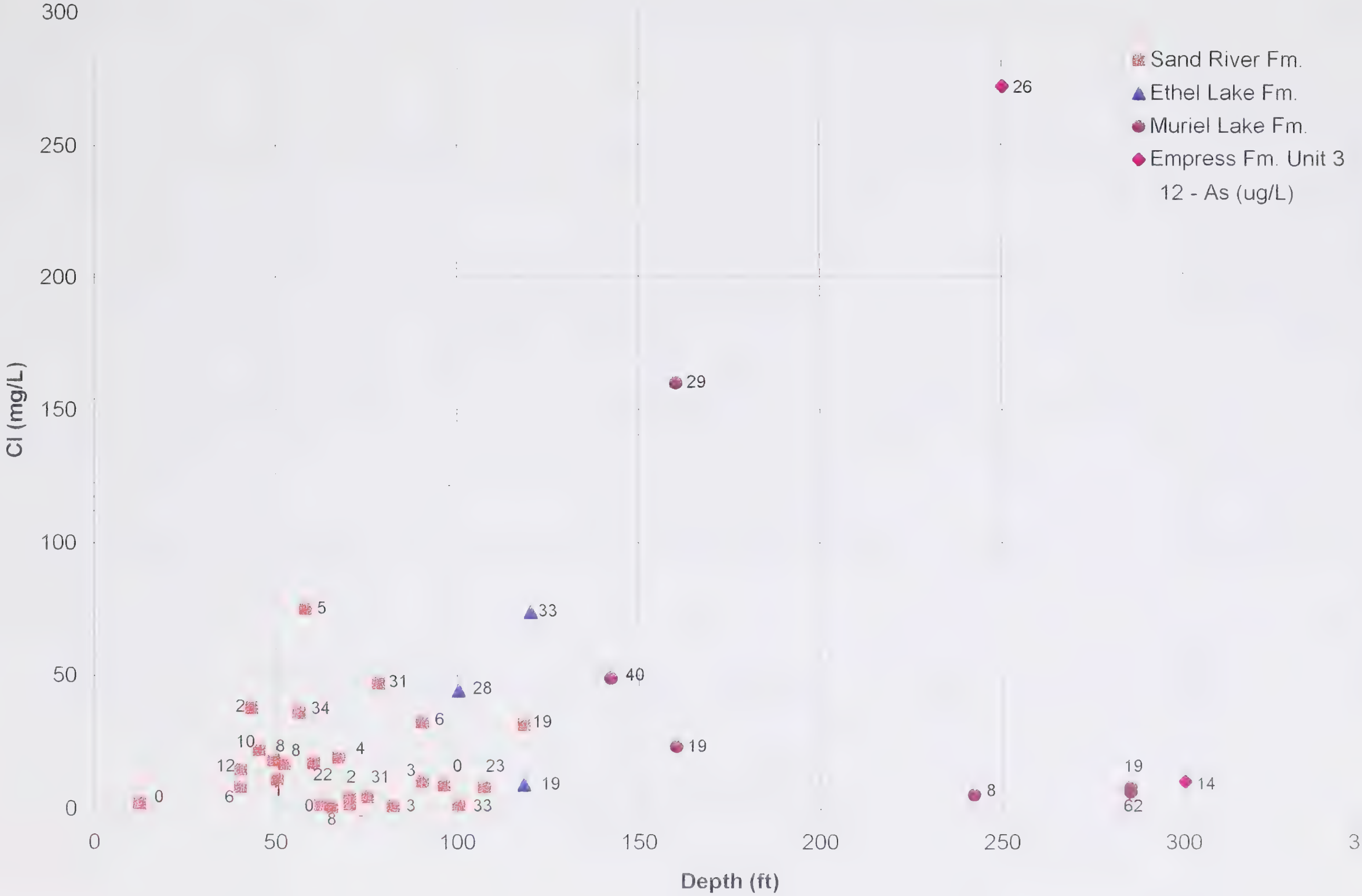
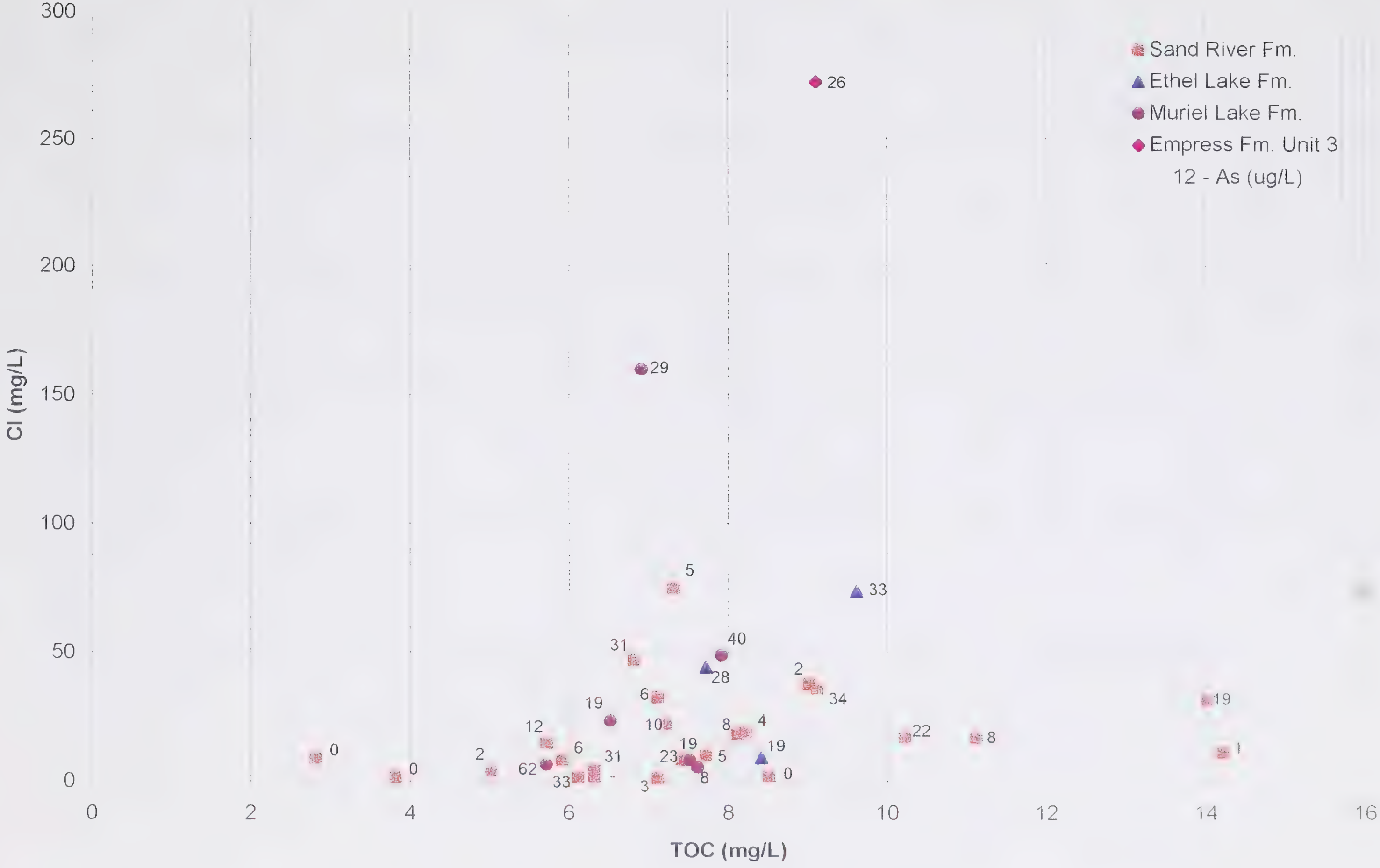


Figure 11
Chloride vs. Total Organic Carbon



in limited supply and the latter if microbial activity had just depleted a large infusion of dissolved organic compounds.

4.7.5 Arsenic, Iron and Redox Potential

It is generally believed that the major geochemical control on the concentration of arsenic in groundwater is pH, redox potential, and iron oxide mineralogy (Nickson et al., 1998). Redox potential is a measure of the oxidizing or reducing conditions of soils, sediments, aquifers, or water. High numerical values, like +600 mV, indicate oxidizing conditions in well-oxygenated environments. Values of −100 mV for example, would indicate oxygen depletion and reducing conditions.

The redox potential and pH manifest their control on arsenic through the dissolution of natural soil minerals that contain arsenic, such as pyrite, and the behavior of secondary iron oxides that contain adsorbed arsenic. On a worldwide basis, including Alberta, groundwaters with high concentrations of native arsenic are commonly associated with the presence of pyritic containing geologic materials of marine origin. High concentrations of arsenic can and do occur in the pyrite mineral structure (Dudas, 1987).

In a high redox potential environment, pyrite can oxidize and release the arsenic that originally was locked within the crystal structure of the sulfide mineral. Once released, the arsenic is strongly adsorbed by secondary iron oxides (Pierce and Moore; 1982) that occur in soils and geologic materials. Oxidation of pyrite also releases iron that subsequently forms secondary iron oxides that have a high adsorption affinity for arsenic and related anions. For well-oxygenated aquifers, these secondary iron oxides are very effective in capturing arsenic and limiting its concentration in groundwater. However, if reducing conditions develop, the secondary iron oxides begin to dissolve, releasing both iron and arsenic into the water phase. Reduction of secondary iron (Fe^{3+}) oxides typical occurs through an Eh range of +100 mV to −100 mV at a pH of about 7.0 (McBride, 1994). Complete reduction and dissolution of secondary iron oxides would be expected if Eh conditions are persistently below − 100 mV.

Figures 13, 14 and 15 illustrate the data for arsenic, iron, and redox potential (Eh) for the water samples of this study. With only one exception (one Ethel Lake sample), the highest arsenic concentrations occur under low redox conditions (Figure 13). All shallow wells in the Sand River Formation with arsenic concentrations in excess of 10 μg/L have field measured redox potentials below –100 mV. A large number of the shallow wells have moderate to strong reducing conditions. Consistent with the geochemical theory mentioned above, there is a general trend for an increase in arsenic concentration with a decrease in redox potential. Variations in the mineralogy (amount of pyrite, secondary iron oxide) of the aquifer where the well is screened and features such as well history, filtration system, and age of well would cause some deviation from an exact correlation between Eh and As.

Data for arsenic and iron in shallow well water samples of the Sand River Formation (Figure 14) show a clustering of low As and low Fe samples with all high arsenic readings greater than about 20 μg/L associated with greater than 3000 μg Fe/L. The highest concentrations of arsenic in the Sand River Formation are always associated with high Fe, again implicating the role of iron oxides in arsenic chemistry. Variations in mineralogy and well characteristics would account for some scatter in the data.

Combined data for iron and arsenic concentrations in well water and redox potential is shown in Figure 15. Theory predicts that all secondary iron oxides would be reduced at a redox potential less than about –100 mV (McBride, 1994). The data show samples with iron in excess of 2500 μg/L have redox potentials near or below –100 mV. These same samples all have relatively high concentrations of arsenic (see boxed area in Figure 15). These data clearly indicate low redox conditions contribute to the dissolution of iron oxides with a subsequent release of adsorbed arsenic into groundwater.

The data for samples from wells screened in the Muriel Lake Formation do not show any relationship between iron and As. This formation must be different mineralogically than the Sand River Formation. The data for iron, arsenic and Eh (Figure15) show most of the highly reduced samples are low in iron yet high in arsenic. These data could be interpreted to mean

Figure 12
January Arsenic vs. Total Organic Carbon

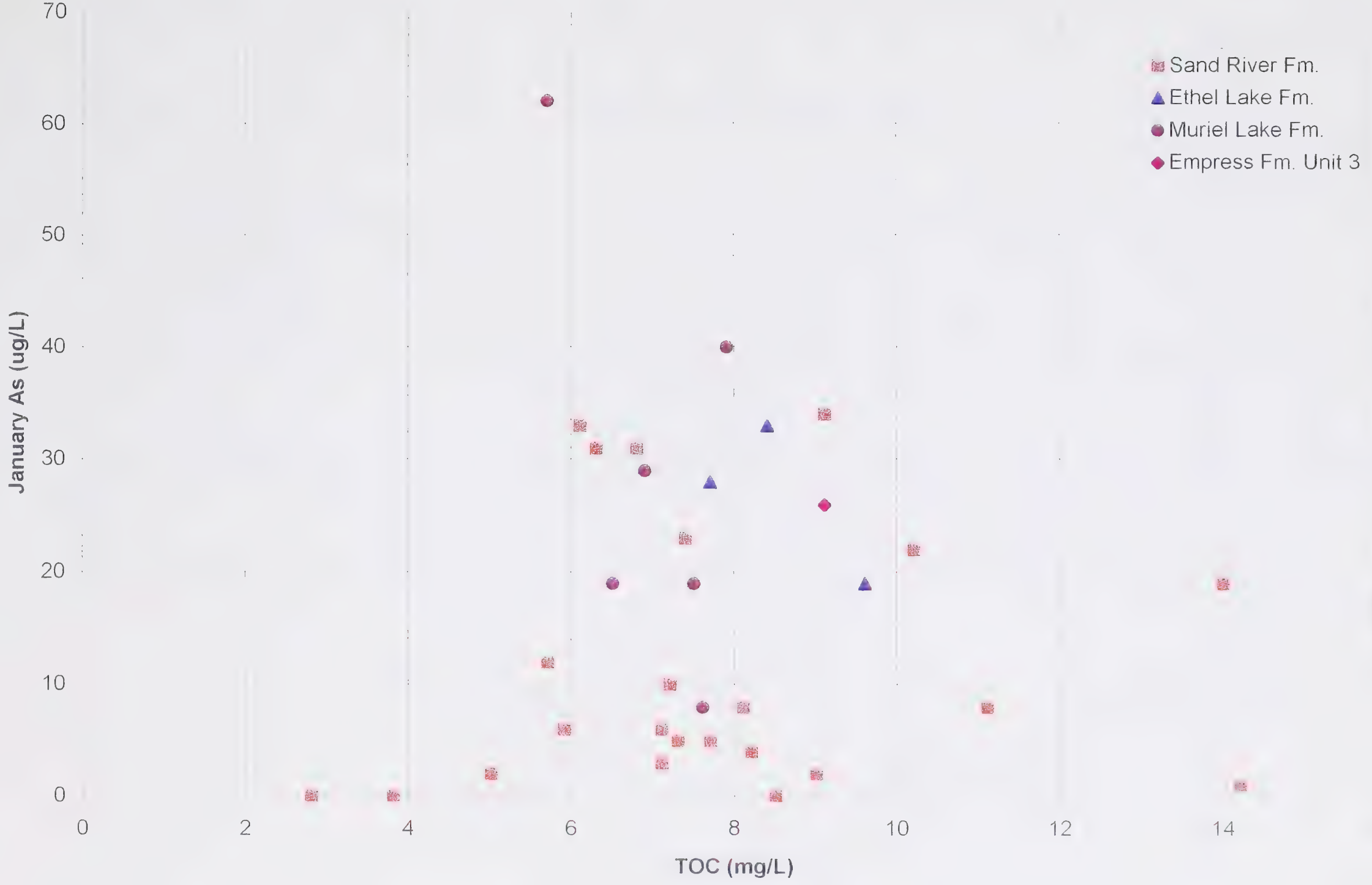


Figure 13
Redox Potential vs. January Arsenic

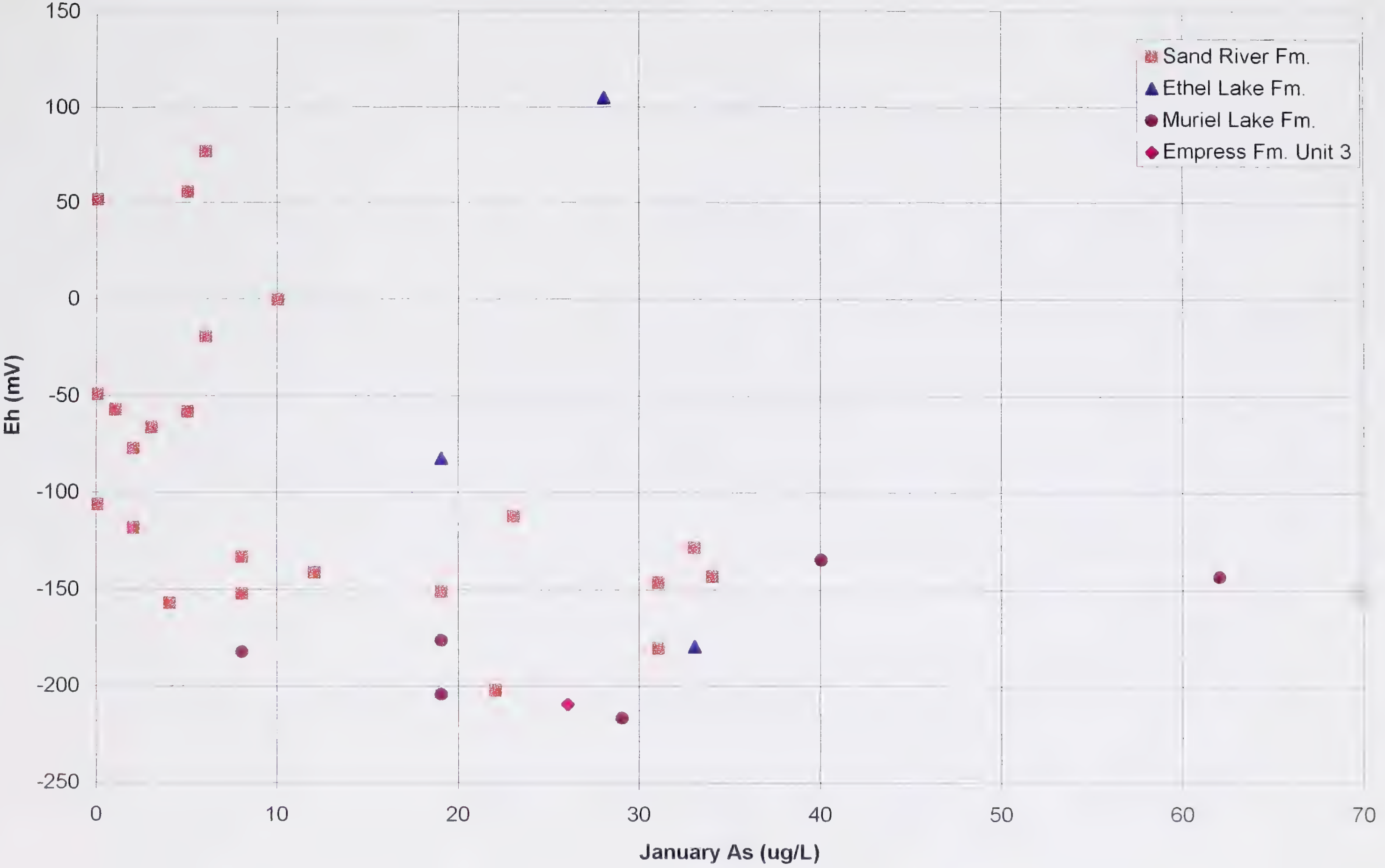


Figure 14
January Arsenic vs. Iron

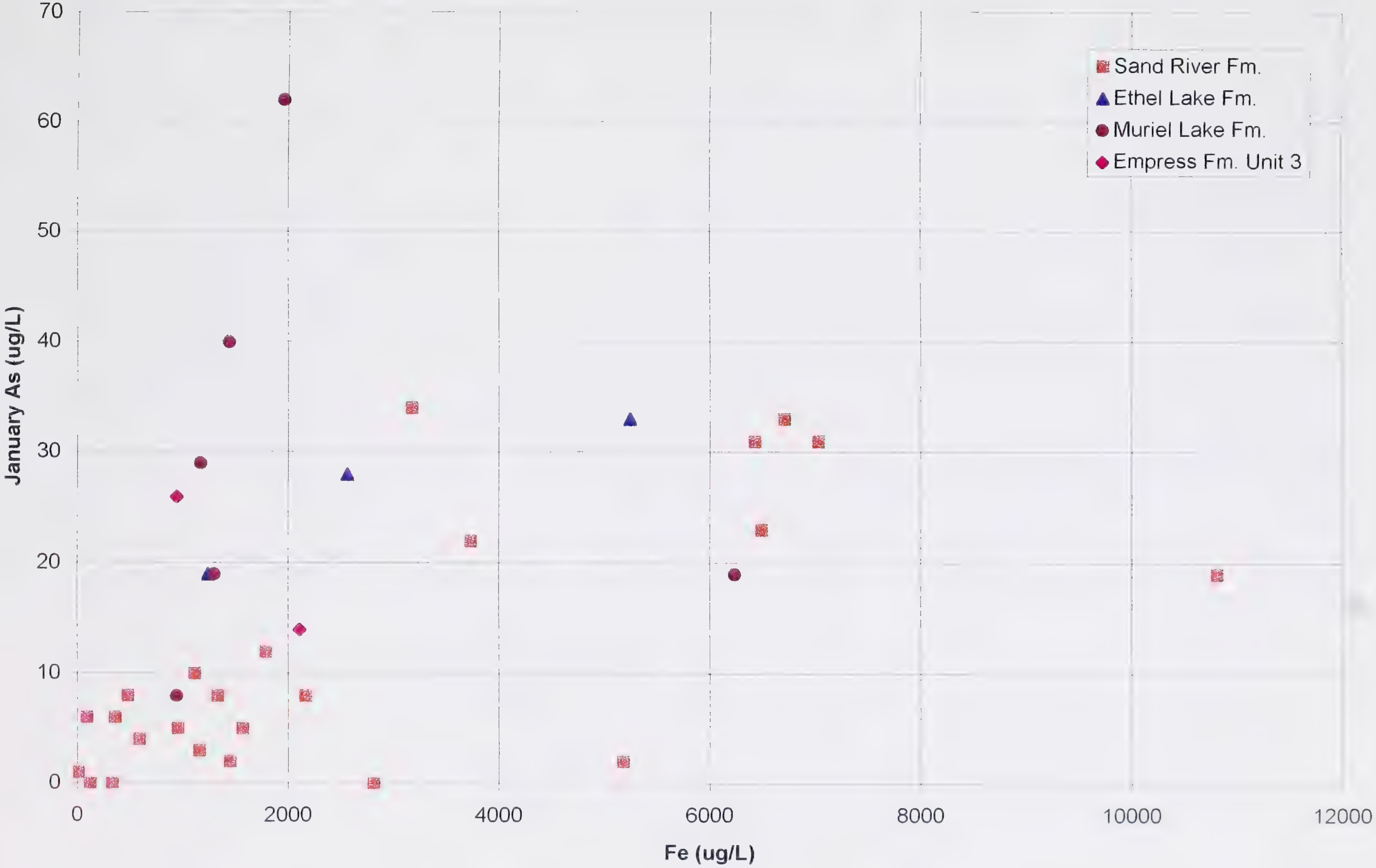
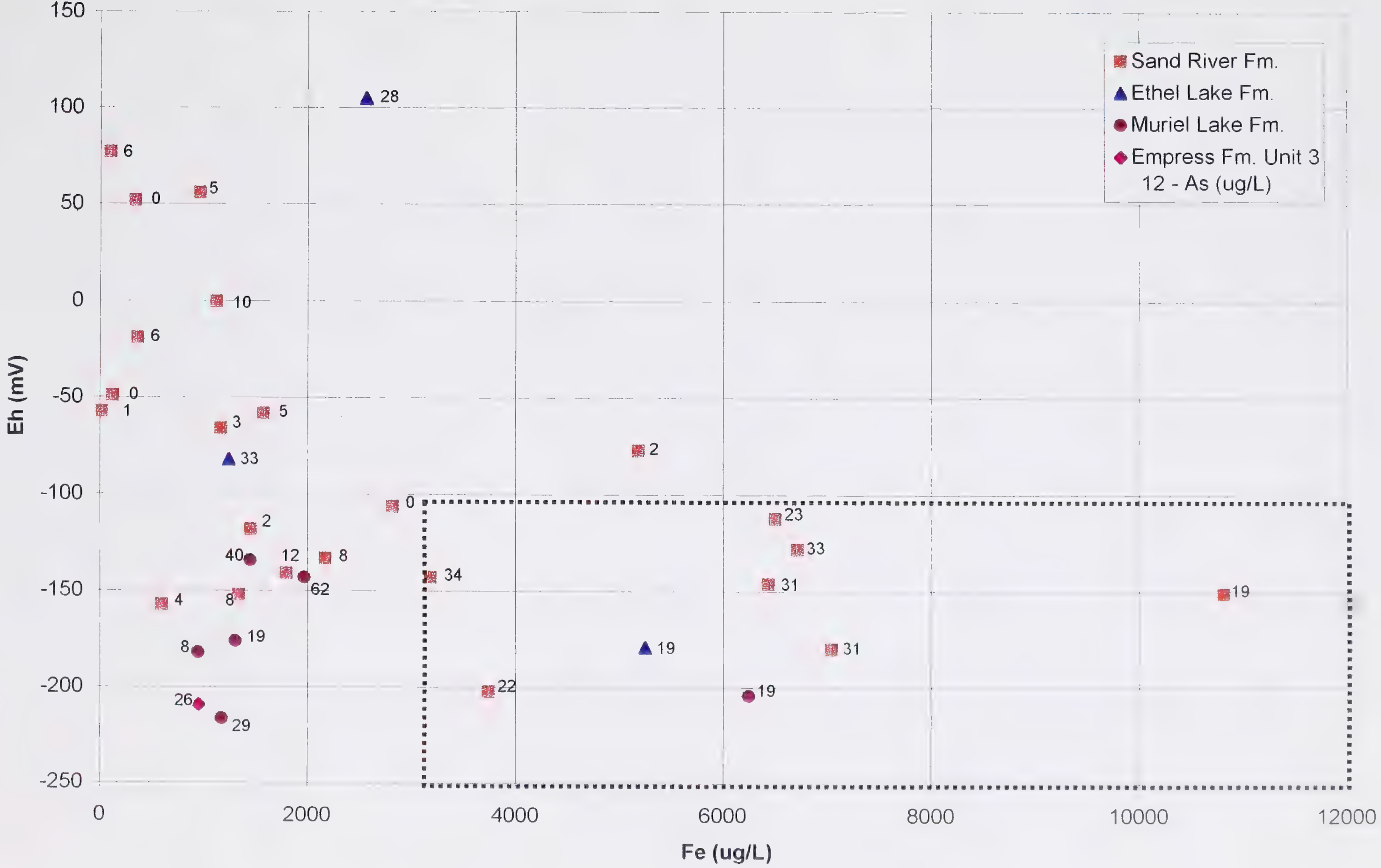


Figure 15
Redox Potential vs. Iron



parts of the Muriel Lake Formation have been depleted of secondary iron oxides yet contain a source of mineral arsenic that maintains the high concentrations in the aquifer. The depletion of secondary iron oxides removes the mineral phase that is most effective in adsorption and removal of arsenic from the water phase.

The results of the chemical analyses of the wells in the Sand River Formation clearly demonstrate that geochemical reactions of iron oxides, driven by the redox potential, have a considerable control on well-water iron and arsenic levels. Heterogeneity in mineral composition, particularly in content of native arsenic bearing minerals like pyrite, within the formation likely also contributes to differences in arsenic concentrations among wells in the area.

5. DISCUSSION

Lithologic and hydrogeologic information, both from the literature and that obtained in this study, were examined to determine the hydrogeologic setting associated with the differences in arsenic concentrations found in shallow wells in the Beaver Lowlands. Particular emphasis was placed on an area located south of Crane Lake, where arsenic concentrations in shallow wells appeared to be greater than elsewhere.

The area is characterized by complex geology, hydrostratigraphy and groundwater flow conditions. The shallow aquifer in which the wells in question are completed is the Sand River Formation which does not physically extend north of Crane Lake.

Deeper aquifers (the Muriel Lake Formation and Empress Formation Unit 3) that underlie the area are, however, much more laterally extensive and do extend to beneath major uplands located to the north.

In the area of high arsenic concentrations in shallow wells, groundwater flow is characterized by dominantly downward movement from the water table to the Sand River Formation, upward

movement from the Muriel Lake Formation, and by lateral movement within the Sand River Formation itself. The data imply that mixing of deep and shallow waters is occurring in the Sand River Formation. However, chloride concentrations in the water indicate that the lateral flux is likely dominant with minimal mixing of deeper groundwater.

No systematic gradients in arsenic concentrations were observed in areas where adequate data existed, implying that local conditions account for the higher level of arsenic observed in shallow wells in the area.

A number of chemical parameters for water samples of this study were measured in order to better understand the basis for elevated concentrations of arsenic, particularly for shallow wells screened in the Sand River Formation. The data show well casing type is not a factor by itself that would account for variation in arsenic. However, well depth does relate to arsenic levels. Deeper wells generally have higher arsenic levels. There is substantial data in this study that indicates redox potential coupled with mineral composition are major parameters that control arsenic concentrations particularly in the shallow wells of the Sand River Formation. High arsenic concentrations were correlated to low redox potential of groundwater. Iron oxides dissolve under these low redox conditions and release native arsenic to groundwaters. Dissolution of the secondary iron oxides also removes the mineral phase that is most effective in maintaining low levels of arsenic in groundwater and in attenuation of the movement of arsenic in the aquifer.

The reason for the low redox conditions in the shallow wells is not apparent from the limited data of this study. Usually, stimulation of microbial activity in the aquifer will result in lowering of the redox potential. The addition of soluble organic compounds to an aquifer is a prime way of microbial stimulation with subsequent lowering of the redox potential. It is possible recharge waters for shallow wells may carry naturally derived dissolved organic substances into the aquifer thereby providing the substrate for microbial activity. Low groundwater flow velocities and slow recharge rates could also contribute to low redox conditions in the Sand River Formation.

This study concludes that there are no systematic gradients in arsenic concentrations with respect to direction of groundwater flow. Variation in the levels of arsenic in the shallow wells of this study appears to be controlled by redox conditions and its influence on iron oxide behavior.

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